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# Development Of GaAs Infrared Window Material

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DEVELOPMENT OF GaAs INFRARED WINDOW MATERIAL

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Prepared by

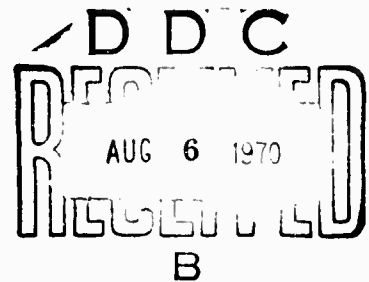
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June, 1970



Submitted to

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ABSTRACT

The choice of window material for the 10.6 micron region and high power carbon dioxide lasers is discussed, and reasons for choosing GaAs given. The theory of semi-insulating GaAs is summarized. The growth, electrical properties and optical properties of chromium-doped GaAs are described with particular reference to the 10.6 micron region. The use of other materials such as GaSb, the refinement of the high-resistivity GaAs and the development of large-diameter boules are considered.

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## 1. INTRODUCTION

With the recent advent of high power carbon dioxide lasers a need has arisen for suitable window materials for the 10.6 micron region. The classical materials for this wavelength region are the halide salts, such as sodium chloride or potassium bromide. While the bulk absorption coefficients of this class of materials are small, their physical properties leave much to be desired. They are hygroscopic, leading to a high surface absorption coefficient, soft and difficult to work. At high power levels they suffer from thermal fracture. Non-oxide glasses formed from the heavy elements show much improved physical properties and can be cast in large sizes. However, their higher absorption coefficient and poor thermal properties lead to thermal runaway and fracture. Semiconductors have excellent physical properties and can be easily worked. Their thermal properties are markedly better than either of the above classes of material. Their absorption coefficients are higher than those of the halide salts, but comparable with the glasses.

Semiconductor materials which can be considered for CO<sub>2</sub> laser window use have to be sufficiently intrinsic or compensated such that significant free-carrier absorption cannot occur. Germanium has been used extensively, but has to be cooled (usually by water) in order to prevent thermal runaway. Of all the other semiconductor materials GaAs and CdTe appear to have the

lowest absorption coefficients at room temperature, and of these two GaAs has superior thermal properties. Further details on the choice of window material for CO<sub>2</sub> lasers, the mechanisms of failure, etc. are given in a review article and a report by a group at Raytheon.<sup>1,2</sup>

Figure 1 shows the predicted behavior of the optical absorption coefficient at 10.6 microns for semi-insulating (Cr-doped) GaAs and three different samples of Ge as a function of temperature. These curves have been replotted from data given in Reference 2. The low temperature values are those measured experimentally, while the behavior with temperature is theoretical with some practical justification. The thermal generation of free carriers is responsible for the very rapid increase in absorption coefficient for temperatures just above room temperature. It is this mechanism which causes thermal runaway in Ge, and why Ge windows must be cooled if the light beam power is high.<sup>1,2</sup> Since GaAs has a band-gap which is twice as large as Ge, thermal excitation is negligible up to 500°K. Its very low absorption coefficient is responsible for less power being absorbed by the window, with a lower resultant temperature rise.

While the mechanical and thermal properties of GaAs are well established, the optical absorption coefficient in the 10.6 micron region is not. The values reported range from 0.006 cm<sup>-1</sup> (References 3 and 4) through 0.012 cm<sup>-1</sup> (Reference 5) and 0.02 cm<sup>-1</sup> (References 1 and 2) up to 0.16 cm<sup>-1</sup>

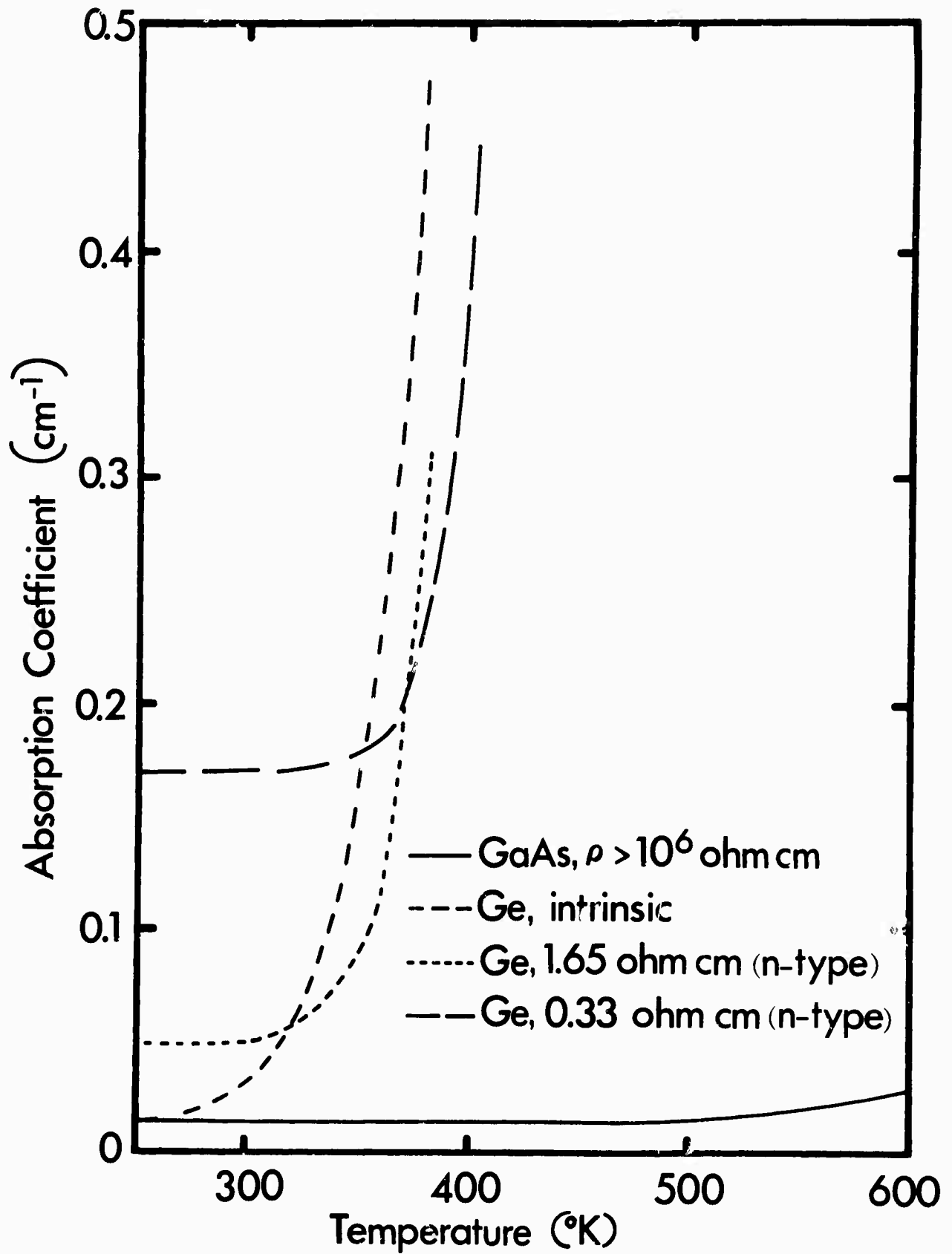


FIGURE 1. The Optical Absorption Coefficient of Ge and GaAs at 10.6 Microns as a Function of Temperature. (References 1 and 2)

(Reference 3). The purpose of this work is to examine the reasons for the large variation, to determine the conditions for the growth of optimized material (i.e. lowest absorption coefficient at  $10.6\mu$  and  $300^{\circ}\text{K}$ ) and to increase the diameter of the ingots so that large windows can be fabricated. In addition GaSb and ultra-pure GaAs, suitably doped, will be investigated as alternate window materials.

## 2. SEMI-INSULATING GALLIUM ARSENIDE

Gallium arsenide typically contains one or two ppma (corresponding to  $2$  to  $4 \times 10^{16} \text{ cm}^{-3}$ ) of electrically active impurities when it is pulled from a melt or boat-grown. This usually results in an n-type carrier concentration on the order of  $2 \times 10^{16} \text{ cm}^{-3}$ . However, if certain dopants are added to the melt or the atmosphere of the apparatus near-intrinsic resistivities can be obtained, ranging from  $10^4$  to  $10^8 \text{ ohm-cm}$  at room temperature. The dopants which have commonly been used are the transition metals such as iron, cobalt and nickel and other elements such as chromium, oxygen, copper and zinc. A brief bibliography of this work is given in Reference 6. It appears likely that all of these elements, with the exception of zinc, produce a deep acceptor level close to the center of the energy gap.<sup>6,7,8</sup> Zinc produces a relatively shallow acceptor, and therefore the amount needed to compensate the dominant n-type impurities is quite critical; this mechanism is assisted by the small amounts of Fe, Cr, etc. which are usually present in GaAs.

The accepted mechanism for the semi-insulating state is based on a model originally proposed by Blanc and Weisberg.<sup>9</sup> They suggested shallow donor and acceptor levels close to the conduction and valence bands respectively, and a deep donor close to the center of the gap. If this deep level is an acceptor rather than a donor, all the observed properties

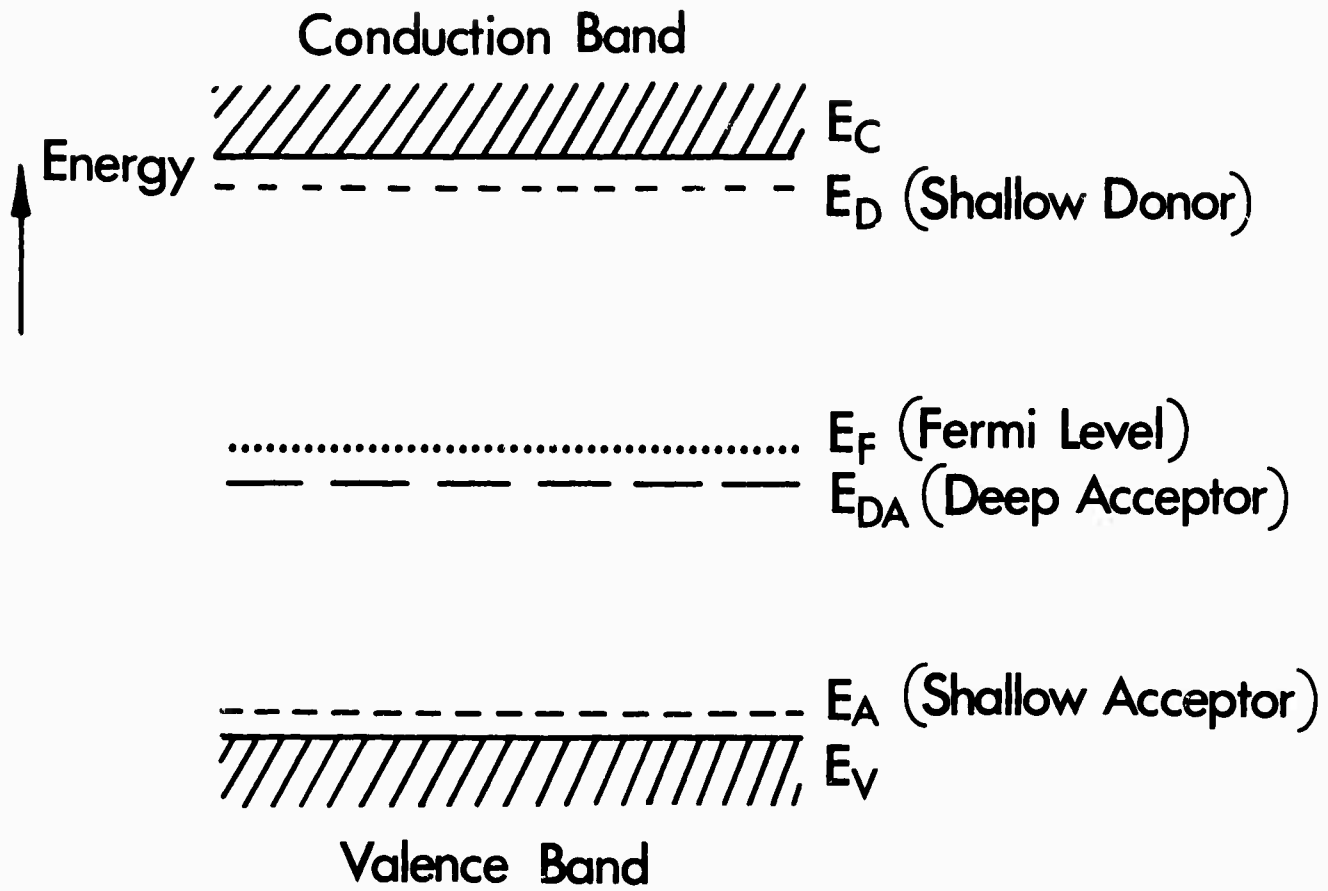


FIGURE 2. Energy Levels at  $K = 0$  in Semi-insulating GaAs, According to a Modified Blanc-Weisberg Model<sup>9</sup> and Experiment.<sup>6,8</sup>

of semi-insulating GaAs can be explained. Figure 2 shows the energy level diagram for GaAs at  $k = 0$ . With this model, the number of deep acceptor impurities only has to exceed  $(N_D - N_A)$  to give essentially intrinsic behavior.<sup>6</sup>

The preparation of semi-insulating GaAs and GaSb is covered in Section 3, while the properties of this material are covered in Section 4.

In cases where extremely low absorption coefficients and good physical and thermal properties are required, other semiconductors, preferably containing heavy elements, might prove superior to GaAs, especially at low temperatures. One of the better candidates is GaSb, and this material will also be investigated on this contract. A major problem here will be to control stoichiometry<sup>10</sup> and doping level to achieve high-resistivity material.

### 3. CRYSTAL GROWTH

The single crystal and polycrystalline material used in this study was prepared by the Czochralski technique. The GaAs was pulled from a melt reacted in an all-quartz sealed system, usually referred to as the Gremmelmaier technique.<sup>11</sup> The GaSb will be pulled from a pre-reacted charge through boric oxide glass, known as the liquid-encapsulation technique.<sup>12,13</sup>

The main features of the sealed system are common to those described by Gremmelmaier,<sup>11</sup> and consist of reacting the charge from the elements within the system, maintaining an atmosphere of arsenic over the melt during growth, R.F. heating and magnetic coupling for seed rotation and height control. A schematic of the equipment is shown in Figure 3. In our system the R.F. is coupled directly to the melt, which is contained in an alumina crucible. All other parts, including the seed holder and bearings are made of high purity fused silica ("quartz").

Gallium of 6N+ purity is loaded into the crucible, and arsenic of 6N+ purity is sublimed into the upper part of the chamber. After flushing with hydrogen and evacuating several times while baking out the entire tube, it is backfilled to 150 torr with helium and sealed. The R.F. generator is then turned on and the melt is heated to a temperature slightly

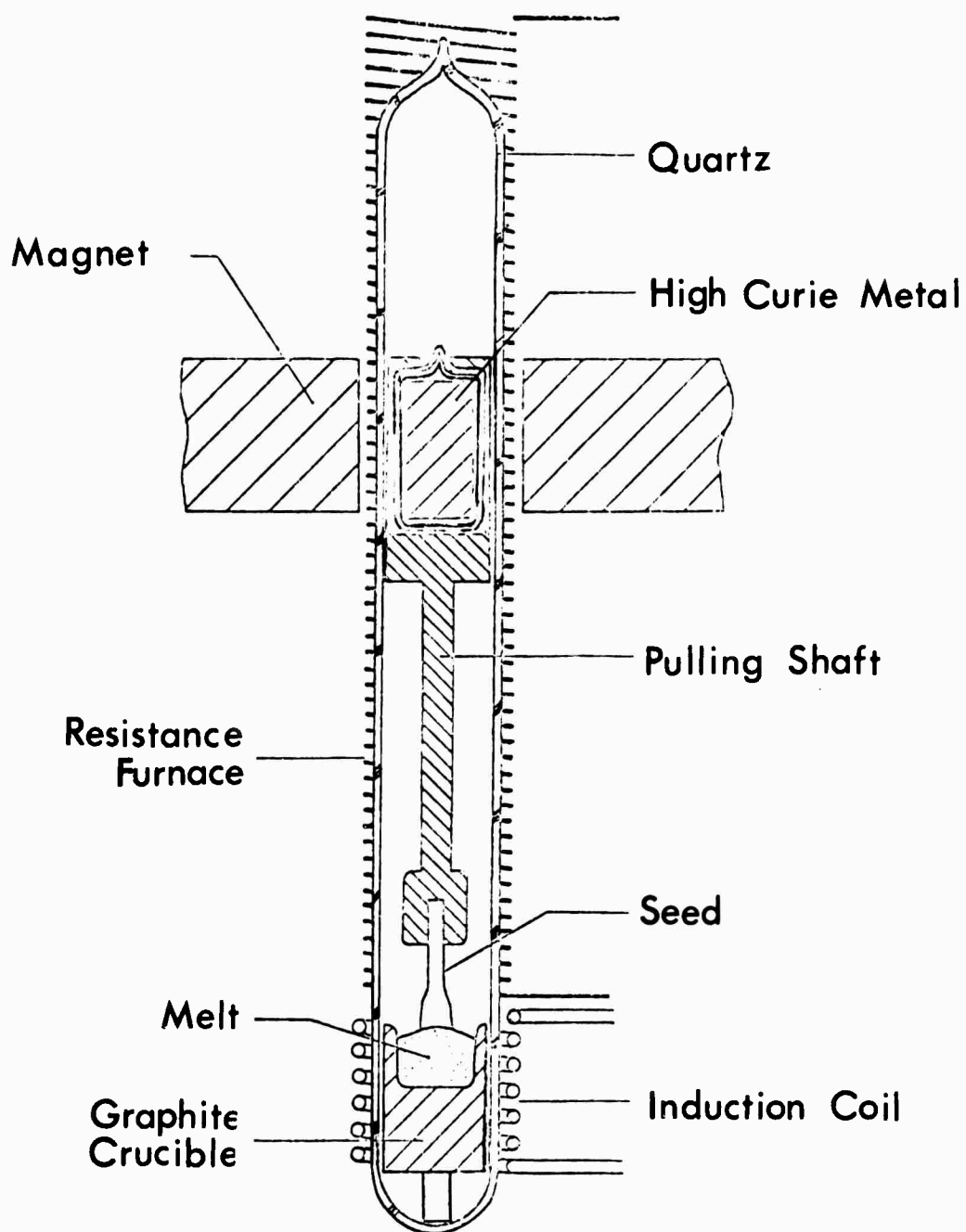


DIAGRAM OF APPARATUS USED FOR PULLING  
CRYSTALS BY THE CZOCHRALSKI TECHNIQUE  
(After Gremmelmaier<sup>11</sup>)

Figure 3

above the melting point of GaAs (which is  $\sim 1240^{\circ}\text{C}$ ). Temperature control of the R.F. is by fully proportional control using a "Ray-o-tube" type of sensor or a sapphire light pipe looking at the bottom of the alumina crucible. The temperature of the resistance heater surrounding the rest of the tube is then slowly increased, subliming the arsenic. It then combines with the liquid gallium until the charge consists of molten GaAs. The temperature of the resistance heaters is then adjusted to give the correct overpressure for the amount of excess arsenic added; this pressure is usually 1.0 to 1.1 atmospheres. A torch is used to keep the viewing window warm enough so that the melt is not noticeably cooler on that side and to prevent arsenic condensation.

After establishing the melting point of the GaAs, the seed is dipped in and growth commences. Diameter control is achieved principally by controlling the temperature of the melt, since the growth rate is usually kept constant between 1.5 and 2 cm hour<sup>-1</sup>. The rotation rate is usually approximately 10 rev min<sup>-1</sup>. Should the initial ingot growth contain grain boundaries or the neck not be of the correct shape or length the seed is lowered, melting far enough back to remove the anomaly. All of the GaAs ingots grown during the course of this work have been {111} oriented, using a positive seed (i.e. the arsenic face is in contact with the melt).

Typical ingot size for the first series of ingots (for the determination

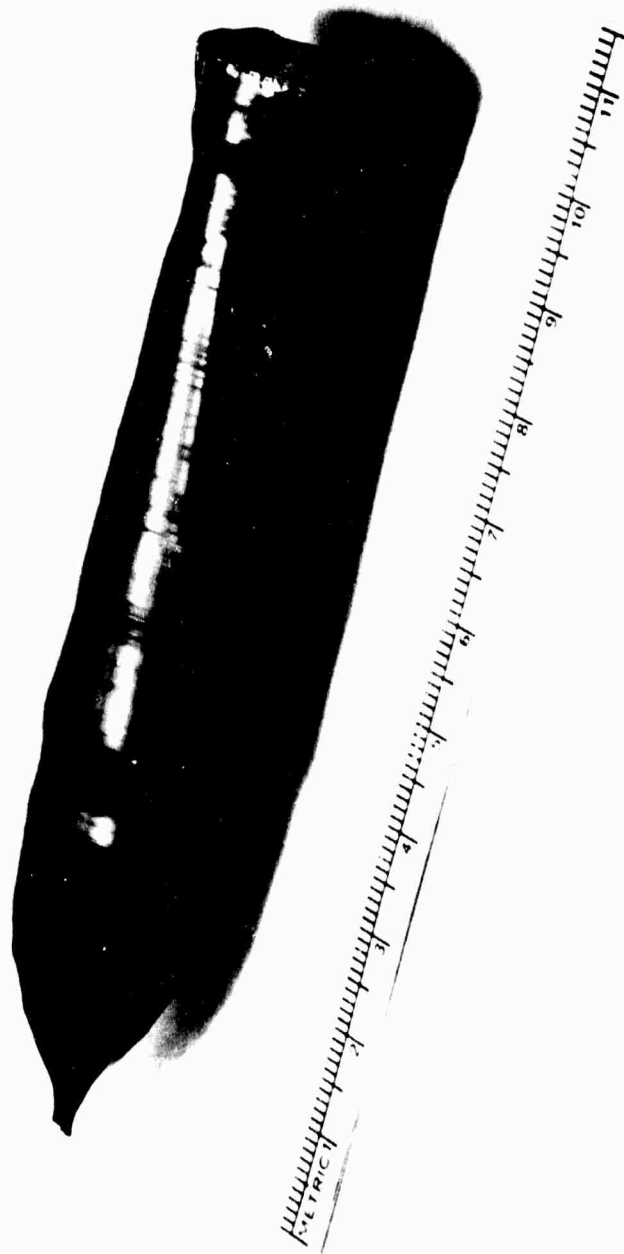


FIGURE 4. A Typical  $\{111\}$  Cr-doped GaAs Single Crystal Ingot

of reproducibility and optimization of chromium content) is 2 to 3 cm diameter and 8 - 12 cm of single crystal length. Figure 4 shows one of these ingots. Features of the ingots are a narrow neck, the three flats above the crown which disappear, and the shape of the growth interface at the bottom.

The gallium antimonide will be grown in the system shown in Figure 5. Here seed rotation and height adjustment, as well as crucible rotation and height are achieved by direct mechanical means operating through pressure seals. The ambient gas or vacuum is contained by the large diameter quartz tube and O-ring seals at each end. Heating is by small semi-cylindrical resistance furnaces supplied by an SCR power supply, which is controlled by a fully proportional temperature controller. The sensing element is a platinum/platinum-rhodium thermocouple mounted close to the windings of the furnace.

During this study fused silica crucibles will be used, with the charge precast in the correct shape. For growth from some types of melt, particularly the antimony-rich ones, boric oxide will be used as an encapsulant. The boric oxide is prepared by heating boric acid in a platinum crucible at 1,000°C for several days. After casting it is baked either in the reaction tube or a special vacuum furnace at 500°C for one or two days. If every trace of water is not removed the boric oxide glass tends to become opaque

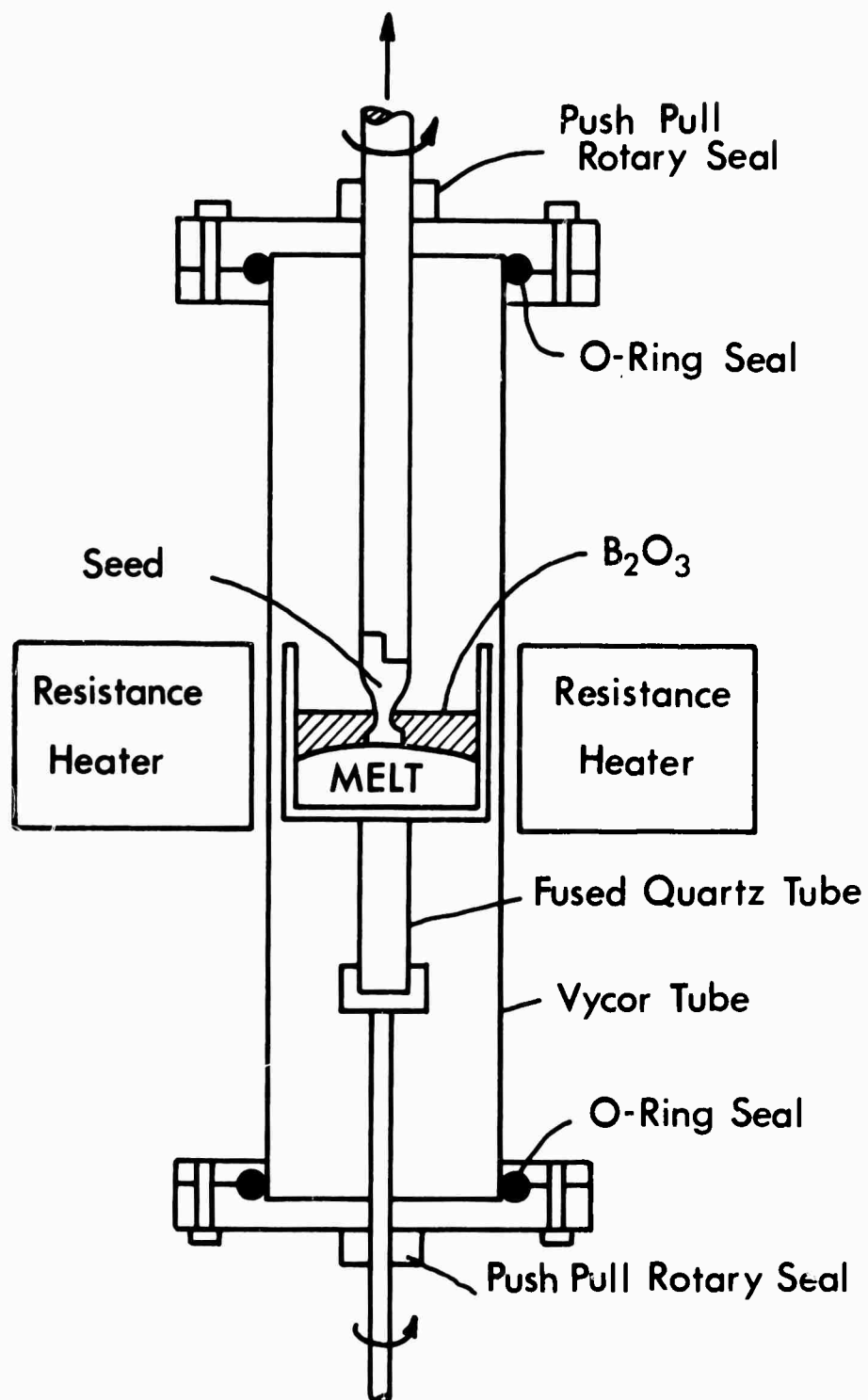


DIAGRAM OF APPARATUS USED FOR PULLING  
CRYSTALS UNDER  $B_2O_3$  GLASS

Figure 5

during crystal growth, resulting in a loss of visibility. For the exposed melt hydrogen is used as an ambient at a pressure slightly greater than atmospheric. For the encapsulated melt nitrogen at 2 to 3 atmospheres is used as the ambient atmosphere.

The crystal growing procedure for GaSb is similar to that described for GaAs. Pull rates of 1.5 to 2 cm hour<sup>-1</sup> are used for growth from stoichiometric melts. A rotation rate of 6 rev min<sup>-1</sup> is used for the seed, while the crucible is not rotated for this material. No single crystal GaSb ingots have yet been produced under this contract.

#### 4. PROPERTIES

The properties of the materials grown under this contract have not yet been analyzed sufficiently to allow their reporting here. However, results on GaAs obtained by ourselves and others prior to the start of the reporting period are summarized here, since they have given direction to this study.

The ingots of GaAs were typically 2 to 3 cm in diameter and up to 12 cm long. Dislocation densities ranged from  $5 \times 10^3 \text{ cm}^{-2}$  at the top of the best ingots to  $2 \times 10^5 \text{ cm}^{-2}$  at the bottom of the poorest ingots. The amount of chromium found in the ingots which were semi-insulating ranged from 0.5 to 5 ppma, as determined from a carefully calibrated spark-source mass spectrometer. The quantity of Cr needed to give resistivities in excess of  $10^6 \text{ ohm-cm}$  at room temperature varied from 0.5 to 2 ppma, yielding qualitative agreement with undoped ingots which usually have excess n-type carrier densities of  $1 - 5 \times 10^{16} \text{ cm}^{-3}$ . Cronin and Haisty<sup>6</sup> came to a similar conclusion, although their mass spectrographically determined chromium contents look low when compared with their radioactively determined values and our mass spectrographic data.

Our value for the distribution coefficient of chromium in pulled crystals of  $6 \times 10^{-4}$  has been discussed previously,<sup>14</sup> and is in agreement with

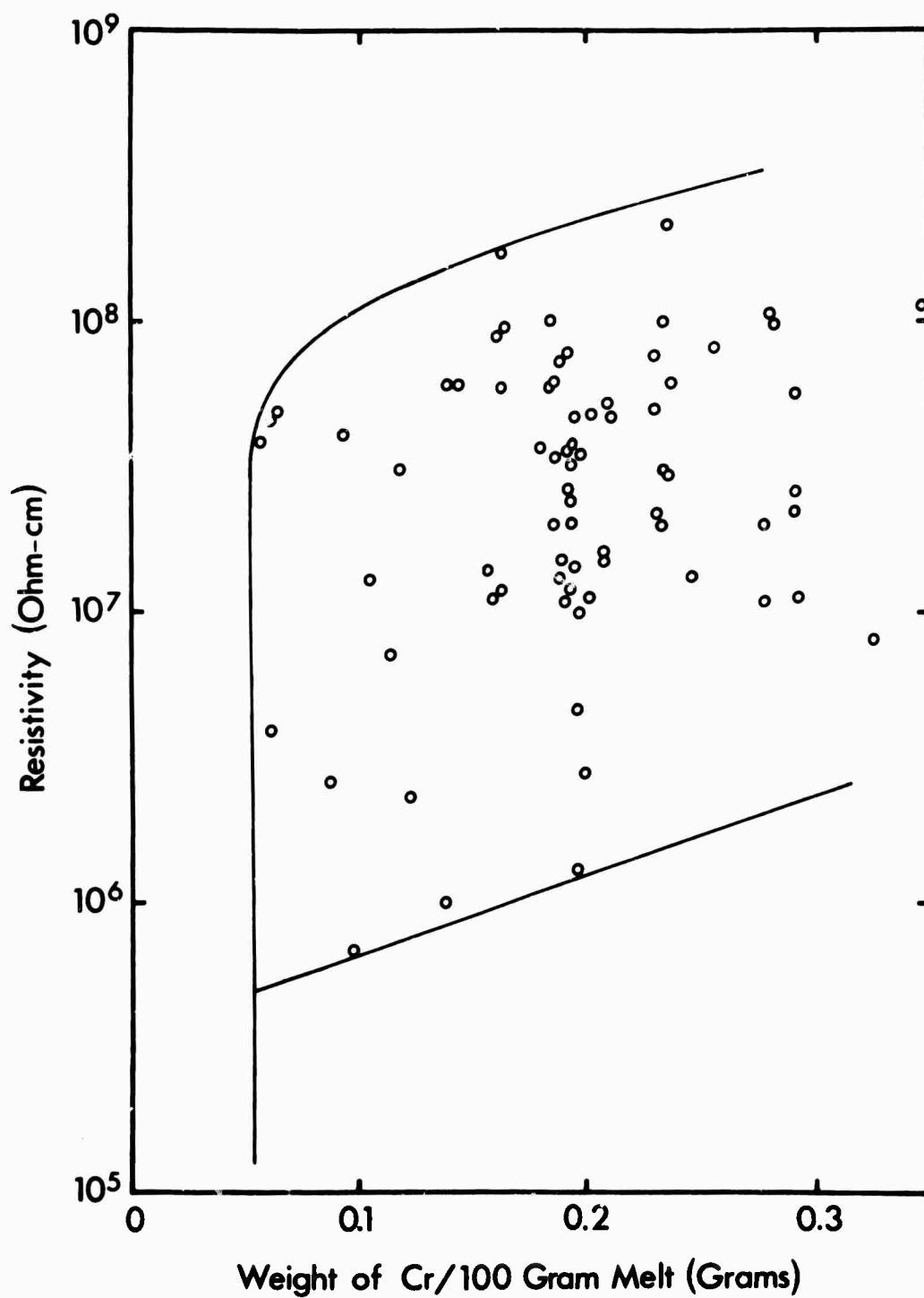


FIGURE 6. The Resistivity of Cr-doped GaAs Ingots as a Function of the Amount of Chromium Added to the Melt. Each Point Represents a Value from the Top of an Ingot.

the literature.<sup>6</sup> Figure 6 shows the room temperature resistivity of Cr-doped GaAs as a function of the amount of Cr added to the stoichiometric GaAs melt. The measurements were taken in the dark on bridge-shaped samples with alloyed indium contacts, using a Tera-ohmmeter. It can be seen that 50 mg of chromium/100 gm of GaAs melt are sufficient to give resistivities in the "semi-insulating range" i.e.  $> 10^6$  ohm-cm. Most of the samples fall between  $10^7$  and  $10^8$  ohm-cm, while the heaviest doped material approaches  $3 \times 10^8$  ohm-cm which is the expected intrinsic resistivity of GaAs at room temperature.

Measurements of the optical absorption coefficient of some of the above GaAs ingots were made at 10.6 microns using a CO<sub>2</sub> laser and a calorimetric technique.<sup>15</sup> Combining these data with those from Reference 4 which were also taken on our material using a similar technique results in a range for  $\alpha(10.6\mu, 300^\circ\text{K})$  of 0.006 to 0.030 cm<sup>-1</sup>. The highest value of this range is comparable with the best values reported for germanium,<sup>1,2</sup> and is twice as good as the best of the hot-pressed family of materials.<sup>1</sup> The lowest and best value reported here is suitable for multi-kilowatt lasers. It can be seen that the higher cost of GaAs versus that of Ge is more than ameliorated by its superior optical properties and its ability to operate without special cooling arrangements.

Figure 7 shows the optical absorption coefficient of our GaAs as a

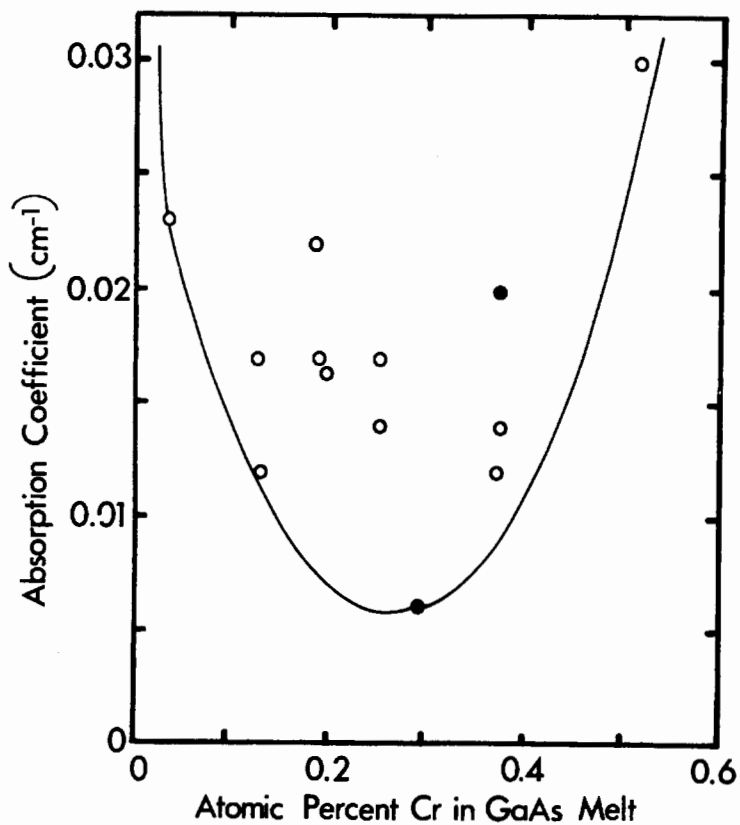


FIGURE 7. The Optical Absorption Coefficient at 10.6 Microns and 300°K of Pulled Cr-doped GaAs as a Function of Chromium Content in the Starting Melt.

function of the chromium concentration in the melt.<sup>4,15</sup> There is a strong indication that there is an optimum amount of Cr which should be added to give the best window material. The wide range of  $\alpha$  for a similar chromium content has to be investigated however.

## 5. FUTURE WORK

The first series of GaAs ingots will be used to determine the absorption coefficient at 10.6 microns as a function of chromium concentration. The samples used in Reference 15 were thin slices taken from the lower part of the ingot, and many had additional dopants or poorly controlled growth conditions. These problems have been avoided here, and the series should yield more consistent results. Also to be investigated are the effects of dislocation density, polycrystallinity and dopant type on the absorption coefficient. The electrical properties will be characterized more thoroughly. The Direct-Imaging Microanalyzer and the Scanning Electron Microprobe will be used to directly investigate the distribution of chromium in the optical samples, while the spark source mass spectrometer will be utilized to accurately establish average chromium contents. The growth of larger diameter material will be investigated.

The properties of Cr-doped high purity GaAs grown from dilute gallium solutions and of high resistivity GaSb will be studied. Both of these materials have been prepared previously in our laboratories, but not in high resistivity form.

6. ACKNOWLEDGMENTS

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## 7. REFERENCES

1. F. Horrigan, C. Klein, R. Rudko and D. Wilson, "Microwaves," p. 68 (Jan. 1969).
2. R. I. Rudko and F. A. Horrigan, AD 693 311 (Sept. 1969).
3. J. Comley, E. Garmire and A. Yariv, J. Appl. Phys. 38, 4091 (1967).
4. V. O. Nikolai and G. W. Gottlieb, Tech. Report AFWL-TR-69-108.
5. R. Weil, J. Appl. Phys. 40, 2857 (1969).
6. G. R. Cronin and R. W. Haisty, J. Electrochem. Soc. 111, 874 (1964).
7. O. Madelung, "Physics of III-V Compounds," Wiley, N. Y., p. 263 (1964).
8. D. R. Heath, P. R. Selway and C. C. Tooke, Brit. J. Appl. Phys., Ser. 2, 1, 29 (1968).
9. J. Blanc and L. R. Weisberg, Nature, 192, 155 (1961).
10. R. K. Willardson, Ann. N. Y. Acad. Sci., 137, 49 (1966).
11. R. Gremmelmaier, Z. Naturforsch., 11A, 511 (1956)
12. E. P. A. Metz, R. C. Miller and R. Mazelsky, J. Appl. Phys. 33, 2016 (1962).
13. J. B. Mullin, B. W. Straugham and W. S. Brickell, J. Phys. Chem. Solids 26, 782 (1965).
14. R. K. Willardson and W. P. Allred, Proc. of First Intl. Symp. on GaAs at Reading, p. 35 (1966).
15. A. G. Thompson, Abstract 143, J. Electrochem. Soc. 117, 102C (1970).

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Crystal Growth						
Impurities						
Electrical Properties						
Optical Absorption						
Infrared Windows						
Carbon Dioxide Lasers						